NOTE

Indian J. Phys. **70A** (5), 645–649 (1996)

IJP A
- an international journal

Molecular complexation in polymers

V P Akhare, D K Burghate and V S Deogaonkar
Shri Shivaji Science College, Amravati-444 603,
Maharashtra, India

Received 28 September 1995, accepted 14 March 1996

Abstract : Ultrasonic and viscosity measurements have been employed to study the molecular complexation between proton donor and proton acceptor molecules of Polyvinyl Chloride (PVC) and Polymethyl Methacrylate (PMMA) molecules respectively. Tetrahydrofuran (THF) has been used as a common solvent. Measurements have been made at three different temperatures 30°, 35° and 40° C Maxima or minima in the properties studied have been used to predict complex formation.

Keywords : Ultrasonic velocity, viscosity, PVC-PMMA

PACS Nos. : 61.41.+e, 43.35.Cg

Few attempts seem to have been made to use acoustics as a tool in studying physical properties of polymers. Degradation of polymers subjected to ultrasonic waves has been reported to occur by Gowarikar *et al* [1]. Velocity of ultrasonic waves has been measured by Swarup and Chandra [2] in Xylene solutions of phenolic and silicon resins and few physical parameters have been calculated. Mallikarjuna Reddy *et al* [3] have measured thermoacoustic properties of polymers at low temperature using theoretical model proposed by Sharma and coworkers [4–7]. Complex formation in polymers by viscosity measurements has been reported by Chaturvedi and Srivastava [8]. The functional groups participate in formation of coordinate covalent bond, namely, the proton donor and proton acceptor groups. Polyvinyl Chloride (PVC) belongs to compounds of proton donor group called as class A [9] while polymethylmetha acrylate (PMMA) belongs to proton acceptor group called as class B [9]. As such, in order to study the interaction between donor-acceptor molecules, samples of PVC and PMMA have been used with tetrahydrofuran (THF) as an inert solvent.

Two polymeric solids namely PVC and PMMA were dissolved in THF, so that the weight fraction of the total solute in THF is of the order of 0.0112. The relative

concentration of the two solutes were changed in definite proportions. Seven samples were prepared and measurements were taken at three different temperatures.

Ultrasonic interferometer has been employed to measure ultrasonic velocity in sample solution at fixed frequency 2 MHz. Viscosity measurements have been made by using an Ostwald viscometer. Temperatures have been kept constant using constant temperature water bath. Density measurements have been made using a density bottle and monopan balance. Accuracy in measurement of ultrasonic velocity is + 0.5%. Temperature can be kept constant to an accuracy of 0.1°C. Accuracy in the measurement of viscosity and density have been ascertained by measuring viscosity and density of known liquids and comparing them with the literature values. Values of ultrasonic velocity, density and viscosity of the samples have been measured at three different temperatures 30°C, 35°C and 40°C. Values of adiabatic compressibility β_a, specific acoustic impedance Z and viscosity η have been calculated using relations :

$$\beta_a = \frac{1}{U^2 \rho}, \tag{1}$$

$$Z_{expt} = U_{expt}\, \rho_{expt}, \tag{2}$$

$$\eta = \frac{(\rho_s - t_s)\, \eta_w}{(\rho_w\, t_w)},$$

where U = Ultrasonic velocity,

η_w = Viscosity of water,

ρ_s = Density of solution,

ρ_w = Density of water,

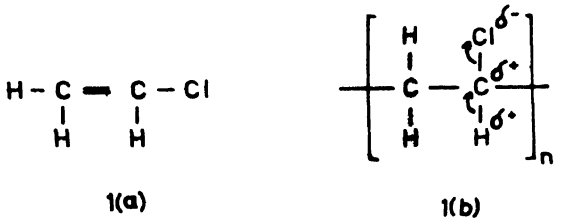
t_s and t_w = Time of fall between specific marks on viscometer for solution and water.

Figures 1(a) and 2(a) represent molecular structure of monomer of PVC and PMMA while Figures 1(b) and 2(b) represent chain structure of PVC and PMMA. The values of η, Z, U and β_a at different temperatures have been plotted against weight fraction of PVC and shown in Figures 3 and 4 respectively.

It can be seen from Figures 3 and 4 that η, Z and U of sample mixtures show a maximum, while β_a shows a minimum at PVC : PMMA = 2 : 1 at all temperatures. Further, the maximum values of velocity U_{max}, viscosity η_{max} and specific acoustic impedance Z_{max} decrease with increase of temperature. Adiabatic compressibility shows an opposite type of behaviour. These experimental observations can be explained on the basis of complex formation through coordinate covalent bonding between the constituents of the mixture.

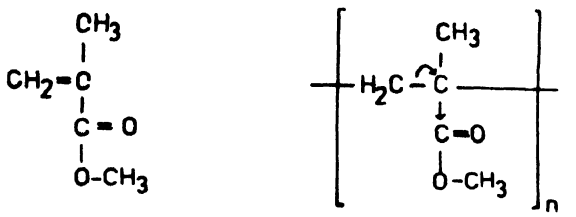
The presence of electro-negative chlorine atom in PVC is responsible for activating the hydrogen atom in the molecule. Chlorine being highly electro-negative attracts the

shared electron pair towards itself creating a partial charge d^+ on C-atom. The carbon atom being attached to hydrogen atom, it will pull the shared electron pair to itself. This makes the H-atom to develope an effective charge d^+, which is the proton available as a donor proton. This is as shown in Figure 1(b).



1(a) 1(b)

Figure 1. (a) Molecular, (b) chain structure of PVC



2(a) 2(b)

Figure 2. (a) Molecular, (b) chain structure of PMMA

Polymethylmethacrylate contains a proton acceptor group (such as ketones, aldehydes, ethers, esters, *etc.*) *i.e.* electron withdrawing ester group.

The presence of electron withdrawing ester group makes the carbon electron-deficient. Hence, this electron deficient carbon pulls the electron pair towards itself and becomes the centre of high electron density for accepting proton. This is as shown in Figure 2(b).

Thus, with the availability of the proton donor group in PVC and proton acceptor group in PMMA, there is likelihood of formation of coordinate covalent bond between PVC and PMMA, giving rise to the complex formation.

It is such complex species which will be statistically expected to be formed in large numbers at PVC : PMMA = 2 : 1 concentrations of the donor acceptor species.

These complex formation might be responsible for the sudden change in the behaviour of the sample mixtures at 2 : 1 concentration.

Strepikheyers *et al* [10] have reported the formation of graft copolymer in polyvinyl acetate with polyethylene in the side chain, polymethyl acrylate with poly-n-chlorostyrene in the side chain, polystyrene with polyvinyl chloride in the side chain.

The bulkier complex containing molecules will naturally exhibit greater viscosity and greater specific acoustic impedance than the individual molecules, giving rise to maximum in η and Z. Similarly, the adiabatic compressibility will decrease with bulkier molecules resulting in a minimum in β_a.

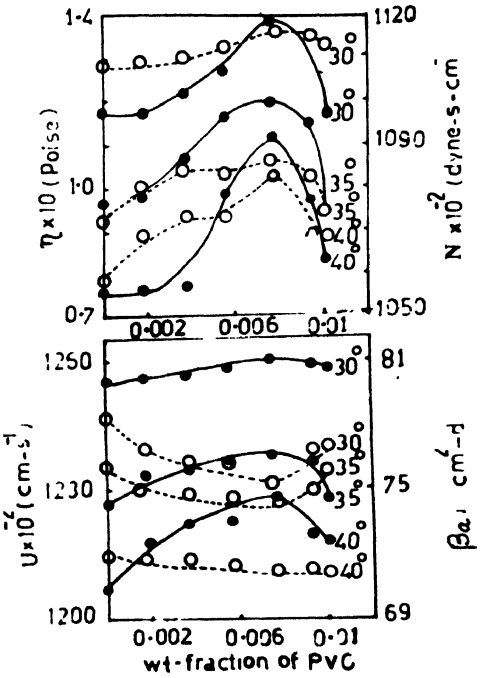


Fig. 3

Fig. 4

Figure 3. Variation of η and Z with weight fraction of PVC

Figure 4. Variation of U and β_a with weight fraction of PVC

Increase in energy of vibration accompanied with rise of temperature should be reflected in a decrement in the maximum values of η, Z and U and increment in the maximum value of compressibility β_a of the sample mixtures.

It therefore, follows that the experimental findings can thus be satisfactorily explained on the basis of complex formation through coordinate covalent bonding between donor and acceptor molecules. Our observations are in agreement with those reported by Tewari *et al* [11].

Acknowledgment

The authors are thankful to Dr. V R Ghurde, the Principal of Shri Shivaji Science College, Amravati for the constant encouragement during progress of the work.

References

[1] V R Gowarikar, N V Viswanathan and J Sreedhar *Polymer Science* (New Delhi . Willey Estern Ltd) p 231 (1956)

[2] S Swarup and S Chandra *J. Polym. Mater.* (India) 5 147 (1988)

[3] P Mallikarjuna Reddy, R Ramkrishna Reddy, Chewdonji Rao and B K Sharma *Indian J Pure Appl Phys* **27** 275 (1989)

[4] B K Sharma *J Acoust Soc Am.* (USA) **73** 106 (1983)

[5] B K Sharma *Acustica* (Germany) **53** 100 (1983), **43** 221 (1979)

[6] B K Sharma and R R Reddy *Indian J. Pure Appl Phys* **23** 396 (1985)

[7] B K Sharma and R R Reddy *J. Polym Mater* (India) **1** 180 (1984)

[8] B Chaturvedi and A K Srivastava *Polymer International* **31** 269 (1993)

[9] A Tager *Physical Chemistry of Polymers* (Moscow . Mir) English Translation p 344 (1978)

[10] A Strepikheyers, V Deravitakaya and G Slonimsky *A First Course in Polymer Chemistry* (Moscow Mir) p 189 (1971)

[11] N Tewari, S Saini, S K Nigam and A K Srivastava *Acta Polym* **39** Nr 12 679 (1988)